

The following references are mentioned for the first time in this Office action (In numbering of references, these also apply to further procedures.):

(1) EP 0 834 370 B1

(2) Göbel, Rudolf: Knowledge Storage Entities Units. 4. Issue, Berlin: People and Knowledge Nationally-owned Publisher, 1989, pp. 86-89. ISBN: 3-06-021707-6.

I.

The subject matters of claims 13 to 15 and 17 are anticipated by reference 1 which would already show an inorganic metal powder having the following features (see e.g. claims 2 and 3):

- the inorganic powder comprises a metal powder of noble metal, nickel, and/or copper coated with at least one metal oxide of titanium oxide, silicon oxide, and/or a rare earth metal oxide (relevant to present claims 13, 15, and 17);
- the inorganic powder particles exist independently without being substantially agglomerated, and the metal oxide coating is deposited with uniform, small thickness without being substantially clustered in the space between the inorganic powder particles (relevant against present claim 14). This would follow from the fact that in reference 1 no agglomeration of the powder particles and no clustering of the metal oxide coating is mentioned.

Reflection in claim 13 on claims 1 to 12 is not recognizable because the reflection does not contribute to rewriting of the claim subject matter according to the category (product) of claim 13.

Therefore, claims 13 to 15 and 17 lack novelty.

II.

Claim 4 has not been recognized so far, which should disclose teachings under protection. First of all, what the concentration ranges "0.1 to

1.5M" etc. mean is unclear even if the description document is present for explanation. The unit "M" does not exist in physical chemistry. An overview about entities and units in physical chemistry is given in reference 2.

Since the present invention according to claim 4 is not so clear and is not completely defined in that those skilled in the art who is here graduate engineer (junior college of technology) for material technology with the knowledge of the field of powder metallurgy and physical chemistry, can execute the present invention, the application must be rejected even though claim 4 is not objected (PatG §48 in connection with §34 paragraph 4).

III.

For the reasons mentioned in I. and II., claims 4, 13 to 15, and 17 are not allowable.

The allowability of the subject matters of claims 1 to 3, 5 to 12, 16, and 18 over the prior art could not be ascertained so far. The applicant is requested to submit relevant claims and the adapted description. When adapting of the description, the false concentration ranges having the non-existent unit "M" can be removed from pages 12, 15, 17, 18, and 20 of the description.

Based on the present text, the allowability of patent is not possible.

Examiner for class B 22 F

Lange

House call: 4623

Enclosures: Gazettes of 2 references

Deutsches Patent- und Markenamt

München, den 30. März 2005

Telefon: (0 89) 21 95 - 3058

Aktenzeichen: 10 2004 008 875.6-24

Anmelder/Inhaber: Samsung Electronics
Co., Ltd.

Deutsches Patent- und Markenamt - 80297 München

Patentanwälte
Ruff, Wilhelm, Beier
Dauster & Partner
Postfach 10 40 36
70035 Stuttgart

Ihr Zeichen: P 43850 DE

Bitte Aktenzeichen und Anmelder/Inhaber bei
allen Eingaben und Zahlungen angeben!

Zutreffendes ist angekreuzt ☒ und/oder ausgefüllt!

Prüfungsantrag, Einzahlungstag am 18. Februar 2004

Eingabe vom

eingegangen am

Die Prüfung der oben genannten Patentanmeldung hat zu dem nachstehenden Ergebnis geführt.

Zur Äußerung wird eine Frist von

vier Monat(en)

gewährt. Die Frist beginnt an dem Tag zu laufen, der auf den Tag des Zugangs des Bescheids folgt.

Für Unterlagen, die der Äußerung gegebenenfalls beigelegt werden (z. B. Beschreibung, Beschreibungsteile, Patentansprüche, Zeichnungen), sind je zwei Ausfertigungen auf gesonderten Blättern erforderlich. Die Äußerung selbst wird nur in einfacher Ausfertigung benötigt.

Werden die Beschreibung, die Patentansprüche oder die Zeichnungen im Laufe des Verfahrens geändert, so hat der Anmelder, sofern die Änderungen nicht vom Deutschen Patent- und Markenamt vorgeschlagen sind, im Einzelnen anzugeben, an welcher Stelle die in den neuen Unterlagen beschriebenen Erfindungsmerkmale in den ursprünglichen Unterlagen offenbart sind.

Hinweis auf die Möglichkeit der Gebrauchsmusterabzweigung

Der Anmelder einer mit Wirkung für die Bundesrepublik Deutschland eingereichten Patentanmeldung kann eine Gebrauchsmusteranmeldung, die den gleichen Gegenstand betrifft, einreichen und gleichzeitig den Anmeldetag der früheren Patentanmeldung in Anspruch nehmen. Diese Abzweigung (§ 5 Gebrauchsmustergesetz) ist bis zum Ablauf von 2 Monaten nach dem Ende des Monats möglich, in dem die Patentanmeldung durch rechtskräftige Zurückweisung, freiwillige Rücknahme oder Rücknahmefiktion erledigt, ein Einspruchsverfahren abgeschlossen oder - im Falle der Erteilung des Patents - die Frist für die Beschwerde gegen den Erteilungsbeschluss fruchtlos verstrichen ist. Ausführliche Informationen über die Erfordernisse einer Gebrauchsmusteranmeldung, einschließlich der Abzweigung, enthält das Merkblatt für Gebrauchsmusteranmelder (G 6181), welches kostenlos beim Patent- und Markenamt und den Patentinformationszentren erhältlich ist.

**Dokumentenannahme
und Nachbriefkasten
nur
Zweibrückenstraße 12**

Hauptgebäude:
Zweibrückenstraße 12
Zweibrückenstraße 5-7 (Breitthof)
Markenabteilungen:
Cincinnatistraße 84
81534 München

Hausadresse (für Fracht):
Deutsches Patent- und Markenamt
Zweibrückenstraße 12
80331 München

Telefon: (089) 2195-0
Telefax: (089) 2195-2221
Internet: <http://www.dpma.de>

Zahlungsempfänger:
Bundeskasse Weiden
BBk München
Kto.Nr.: 700 010 54
BLZ: 700 000 00
BIC (SWIFT-Code): MARKDEF1700
IBAN: DE84 7000 0000 0070 0010 54

P 2401.1
1.04 S-Bahnanschluss im
Münchner Verkehrs- und
Tarifverbund (MVG):



Zweibrückenstr. 12 (Hauptgebäude):
Zweibrückenstr. 5-7 (Breitthof):
S1 - S8 Haltestelle Isartor

Cincinnatistraße:
S2 Haltestelle Fasangarten

In diesem Bescheid sind folgende Entgegenhaltungen erstmalig genannt. (Bei deren Nummerierung gilt diese auch für das weitere Verfahren):

(1) EP 0 834 370 B1

(2) Göbel, Rudolf: Wissenspeicher Größen Einheiten. 4. Aufl. Berlin: Volk und Wissen Volkseigener Verlag, 1989, S. 86 – 89. ISBN: 3-06-021707-6

I.

Durch (1) ist bereits ein anorganisches Metallpulver bekannt, das übereinstimmend mit den Gegenständen der Patentansprüche 13 bis 15 und 17 folgende Merkmale aufweist (vgl. Ansprüche 2 und 3):

- Anorganisches Pulver der Metalle Edelmetall, Nickel und/oder Kupfer ist mit den Metalloxiden Titanoxid, Siliziumoxid und/oder einem Oxid der seltenen Erden beschichtet (zu den Ansprüchen 13, 15 und 17).
- Die anorganischen Pulverpartikel liegen ohne wesentliche Agglomeration vor und die Metalloxidbeschichtung ist gleichmäßig dünn und ohne wesentliche Clusterbildung im Zwischenraum zwischen den anorganischen Pulverpartikeln (zum Anspruch 14). Dies ergibt sich daraus, dass in (1) die Agglomeration der Pulverpartikel und die Clusterbildung der Metalloxidbeschichtung nicht erwähnt sind.

Die Rückbeziehung im Patentanspruch 13 auf die Patentansprüche 1 bis 12 ist unbeachtlich, da sie nichts zur Umschreibung der Anspruchsgegenstands gemäß dessen Kategorie (Erzeugnis) beiträgt.

Damit sind die Patentansprüche 13 bis 15 und 17 nicht mehr neu.

II.

Der geltende Patentanspruch 4 lässt bisher nicht erkennen, welche Lehre unter Schutz gestellt werden soll. Unklar ist vor Allem, auch wenn man die Beschreibungsunterlagen zur Erläuterung heranzieht, was mit den Konzentrationsangaben „0,1 M bis 1,5 M“ usw. gemeint sein soll. In der physikalischen Chemie existiert die Einheit M nicht. In der Druckschrift (2) wird ein Überblick über die Größen und Einheiten der physikalischen Chemie gegeben.

Da demnach die Erfindung gemäß Patentanspruch 4 nicht so deutlich und vollständig offenbart ist, dass ein Fachmann, hier ein Dipl.-Ing. (FH) für Werkstofftechnik mit Kenntnissen auf dem Gebiet der Pulvermetallurgie und der physikalischen Chemie, sie ausführen kann, muss die Anmeldung zurückgewiesen werden, wenn der Patentanspruch 4 nicht fallen gelassen wird (PatG § 48 in Verbindung mit § 34 Abs. 4).

III.

Aus den unter I. und II. genannten Gründen sind die Patentansprüche 4, 13 bis 15 und 17 nicht gewährbar.

Ein der Patentfähigkeit der Gegenstände der Patentansprüche 1 bis 3, 5 bis 12, 16 und 18 entgegenstehender Stand der Technik konnte bisher nicht ermittelt werden. Der Anmelderin wird anheim gestellt, hierauf gerichtete Patentansprüche und eine angepasste Beschreibung einzureichen. Bei der Anpassung der Beschreibung sind auf den Seiten 12, 15, 17, 18 und 20 die falschen Konzentrationsangaben mit der nicht existierenden Einheit M zu entfernen.

Mit den vorliegenden Unterlagen ist die Erteilung des Patents nicht möglich.

Prüfungsstelle für Klasse B 22 F

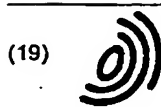
Lange

Hausruf: 4623

Anlagen: Abl. v. 2 Entgegenhaltungen

Hf

P43 850 DE



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 834 370 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.01.2002 Bulletin 2002/03

(51) Int Cl.7: B22F 1/02, B22F 9/30,
H01C 17/065

(21) Application number: 97116642.6

(22) Date of filing: 24.09.1997

(54) Coated metal powder and process for preparing the same by decomposition
Beschichtetes Metallpulver und Verfahren seiner Herstellung durch Zersetzung
Poudre métallique revêtue et sa préparation par décomposition

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: 02.06.1997 JP 15734197
25.09.1996 JP 27292496
26.05.1997 JP 14994997

(43) Date of publication of application:
08.04.1998 Bulletin 1998/15

(73) Proprietor: SHOEI CHEMICAL INC.
Tokyo (JP)

(72) Inventors:
• Asada, Eiichi
Shinjuku-ku, Tokyo (JP)
• Akimoto, Yuji
Shinjuku-ku, Tokyo (JP)

• Shimizu, Fumiyuki
Shinjuku-ku, Tokyo (JP)
• Nagashima, Kazuro
Shinjuku-ku, Tokyo (JP)

(74) Representative: Sandmair, Kurt, Dr. Dr.
Patentanwälte Schwabe, Sandmair, Marx
Stuntzstrasse 16
81677 München (DE)

(56) References cited:
EP-A- 0 067 474 EP-A- 0 088 992
EP-A- 0 091 109 SU-A- 799 914

• PATENT ABSTRACTS OF JAPAN vol. 016, no.
541 (M-1336), 11 November 1992 & JP 04 202602
A (MITSUBISHI PETROCHEM CO LTD), 23 July
1992,

EP 0 834 370 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

BACKGROUND OF THE INVENTION5 1. Field of the Invention

[0001] The present invention relates to a novel metal powder suitable particularly for a thick film paste and a process for preparing the same, and also to a conductor paste using the metal powder and a multilayer electronic component or a multilayer substrate comprising a conductor formed using the paste.

10 2. Description of the Prior Art

[0002] In the field of electronics, thick film pastes, such as conductor pastes and resistor pastes, have been used for the production of electronic circuits and components, such as resistors, capacitors, and IC packages. The thick film paste is prepared by homogeneously mixing and dispersing a conductive powder, such as a metal, an alloy, or a metal oxide, optionally together with a vitreous binder or other additive(s), in an organic vehicle to prepare a paste. It, after application onto a substrate, is fired at a high temperature to form a conductor film or a resistor film.

[0003] Conductive metal powders which are commonly used in the conductor paste or the resistor paste include powders of noble metals, such as silver, gold, platinum, and palladium, and base metals, such as copper, nickel, cobalt, iron, aluminum, molybdenum, and tungsten, or alloys of the above metals.

[0004] Among them, in particular, base metal powders are likely to be oxidized during firing and, hence, heated in an oxidizing atmosphere, up to the step of removing the binder at a temperature of usually about 300 to 600°C, to completely burn out the organic vehicle in the paste. Thereafter, they are fired in an inert or reducing atmosphere, such as nitrogen or hydrogen-nitrogen, and, if necessary, the metal, which has been oxidized at the step of removing the binder, is subjected to reduction treatment. However, oxidation of the base metal to some extent is unavoidable even by the above method, resulting in deteriorated conductivity and soldability. Further, reduction as the post treatment and strict control of the atmosphere and firing parameters are necessary, leading to complicated process and increased cost. Therefore, at least the oxidation of the metal powder in the step of removing the binder in an oxidizing atmosphere should be minimized.

[0005] In multilayer ceramic electronic components, such as multilayer capacitors, an unfired dielectric layer and an internal conductor paste layer are alternately put on top of the other to form a plurality of layers, and these layer are then co-fired at a high temperature. In this case, ceramics used as a dielectric material, such as barium titanate, titanium oxide, and a composite perovskite containing lead, when fired in a reducing atmosphere, causes oxygen deficiency, frequently resulting in deteriorated dielectric properties, which poses a reliability problem. Therefore, firing in an oxidizing atmosphere is preferred until the temperature reaches a value at which the ceramic layer is sintered and densified. For this reason, the development of a base metal paste as an internal conductor material, which can be fired in an oxidizing atmosphere, has been desired in the art.

[0006] On the other hand, also in the case of a noble metal powder, when a metal (for example, palladium or palladium alloy), which is oxidized at a relatively low temperature and then is reduced by further heating to a higher temperature, is used as an internal conductor of a multilayer ceramic component or as an internal wiring conductor of a multilayer ceramic substrate, volume expansion of the electrode derived from oxidation of the metal and subsequent reduction shrinkage occur during firing. It is known that this volume change is not coincident with the shrinking behavior in the sintering of the ceramic layer and, hence, is likely to cause delamination and cracking. This problem occurs also in the case of the above easily oxidizable base metals, such as copper and nickel. Therefore, in both the noble metal and base metal, the oxidation and reduction of the metal powder during the firing is preferably inhibited as much as possible.

[0007] As described in Japanese Patent Publication No. 16041/1985 and Japanese Patent Laid-Open Nos. 131405/1988 and 194137/1990, addition of an element or a metal oxide, which is selectively oxidized during firing, to a conductor paste has been attempted to prevent the oxidation of the metal powder. Depending upon the mixed state of the paste, however, the additive does not effectively act on the surface of the metal powder. Therefore, when the amount of the element or the metal oxide is small, the antioxidation effect is unsatisfactory. On the other hand, addition of a large amount of the element or the metal oxide leads to deteriorated conductivity and soldability and increased impurities to deteriorate the properties of electronic components. Further, the metal oxide produced during firing inhibits sintering of the resultant conductor, often making it impossible to provide a conductor film having satisfactorily low resistance.

[0008] Further, there is a method, as described in Japanese Patent Laid-Open No. 120640/1979, wherein an element, which is preferentially oxidized to form a vitreous material, such as carbon, boron, silicon or aluminum, is alloyed with a conductive metal. Since, however, the alloying element remains in the conductor film after the firing, increasing the resistivity of the resultant conductor. Further, vitrification during the firing requires heat treatment at a temperature considerably above the softening temperature of the glass, making it difficult to control firing conditions and the regu-

lation of the composition and amount. Further, at the present time, there are few processes which can efficiently prepare a fine alloy powder of a submicron size necessary for a reduction in thickness of the conductor layer and a reduction in resistance.

5 [0009] Japanese Patent Laid-Open No. 43504/1992 proposes a method wherein the surface of a metal powder is coated with a metal oxide. This method, however, is unsatisfactory in the antioxidation effect. Further, during the firing, the metal oxide inhibits the sintering of the metal powder. Furthermore, as a matter of fact, it is difficult to effectively coat the surface of the fine metal powder with the metal oxide, and strong aggregation is often created under some treatment conditions.

10 [0010] The Russian document SU 799914 B discloses a magnetic abrasive powder comprising an iron metal nucleus and also comprising a first glassy (vitreous) coating which is again coated with metallic iron. Thus, the document discloses iron metal core particles comprising a vitreous thin layer only as an intermediate product. The final product comprises an additional iron coating. The material disclosed in the document is used as an abrasive powder for polishing surfaces. Nothing is taught about a possible use of the powders for conductive pastes.

15 [0011] EP-A-0 088 992 discloses iron based core particles comprising a vitreous layer. The vitreous layer is formed by partially oxidizing the surface of the core particle and in addition optionally further coating the core particle by providing separate coating material. Following the process of the document the vitreous layer is thus necessarily identical or similar in composition to the core material, which is oxidized to form the vitreous coating. This core material essentially comprises iron.

20 [0012] EP-A-0 067 474 discloses a resistive paste comprising Ag-Pd particles provided with a metal oxidic compound layer.

SUMMARY OF THE INVENTION

25 [0013] An object of the present invention is to provide a metal powder which is highly resistant to oxidation not only during storage of the powder but also in the form of a paste or during firing of the paste and, in particular, during firing, is not oxidized until the temperature reaches a value at which at least the organic vehicle is fully burned out and removed.

[0014] Another object of the present invention is to provide a metal powder which does not undergo oxidation until the sintering at a high temperature is completed, preferably enables firing to be conducted in an oxidizing atmosphere while controlling the sintering behavior of the metal and, in addition, when used in multilayer components, does not create defects such as delamination and cracking.

30 [0015] A further object of the present invention is to provide a simple and improved process for preparing such a powder.

[0016] According to one aspect of the present invention, there is provided a process for preparing a metal powder having a vitreous thin layer on at least a part of the surface thereof, comprising the steps of: bringing a solution comprising at least one heatdecomposable metal compound to fine droplets; and heating the droplets to a temperature above the decomposition temperature of the metal compound, wherein at least one precursor of an oxide, heatdecomposable to produce a vitreous material which, together with the metal, does not form a solid solution, is added to the solution and the vitreous material is deposited, upon the heating, in the vicinity of the surface of the metal powder. According to another aspect of the present invention, there is provided a metal powder obtained by the above process and having a vitreous thin layer on at least a part of the surface thereof.

40 [0017] The metal powder is selected from the group consisting of a noble metal, copper, nickel, cobalt, aluminum, molybdenum, or tungsten and alloys, except iron alloys, or mixtures thereof.

[0018] In the present invention, the amount of the vitreous thin layer in the metal powder with a vitreous thin layer is preferably 0.01 to 50% by weight based on the metal powder excluding the vitreous thin layer. Throughout the specification, the amount of the vitreous thin layer is indicated based on the metal powder (excluding the vitreous thin layer), i.e., the weight of the major metal of the powder, unless otherwise specified.

45 [0019] Further, the present invention provides a conductor paste comprising the above metal powder having a vitreous thin layer on at least a part of the surface thereof and a multilayer ceramic electronic component comprising a conductor layer formed using the paste.

50

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] The present invention will be described in more detail.

55 [0021] In the present invention, the term "metal powder" refers to not only a powder of a simple metal but also an alloy powder.

[0022] The vitreous thin layer, when is present on the surface of the metal powder, functions as a layer for protecting the metal against oxidation. The vitreous thin layer according to the present invention may be an amorphous layer or may be a crystal-containing amorphous layer so far as it has a glass transition point and a glass softening point and

can be fluidized at a high temperature. There is no need for the vitreous thin layer to cover the whole surface of the metal powder, and the deposition of the vitreous thin layer in an effective amount suffices for the contemplated effect. Specifically, the amount of the vitreous thin layer is about 0.01 to 50% by weight based on the metal powder.

5 [0023] The component forming the vitreous thin layer produces oxides, which are, after heat decomposition, hardly dissolved in the metal powder and can be vitrified under metal powder producing conditions according to the process of the present invention. Examples of such components may be at least one member selected from the group consisting of glass components commonly used as inorganic binders in thick film pastes, for example, oxides of elements, such as silicon, boron, phosphorus, germanium, tin, lead, bismuth, alkali metals, alkaline earth metals, copper, zinc, cad-

10 mium, aluminum, indium, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rare earth elements, iron, and cobalt.

[0024] The composition and physical properties (e.g., softening point) of the vitreous thin layer may be suitably regulated according to the kind and applications of the paste. Preferably, in the firing of the paste, the vitreous thin layer is not softened and fluidized until the temperature reaches at least the decomposition temperature of the vehicle. This enables the vehicle to be fully oxidation decomposed and driven off without oxidizing the metal powder even in

15 an oxidizing atmosphere.

[0025] When the softening point of the glass is properly regulated by controlling the composition, the glass does not inhibit the sintering of the metal powder at a high temperature and rather accelerates the sintering at the high temperature. Specifically, as with a glass powder usually incorporated as an inorganic binder in a paste, a glass, which, after the step of removing the binder, is softened at a relatively low temperature, such as lead borosilicate, lead zinc borosilicate, lead aluminum borosilicate, lead cadmium borosilicate, bismuth borosilicate, lead borate, lead zinc borate,

20 and lead germanate, is rapidly softened and fluidized to function as a sintering aid.

[0026] When use of the paste in an internal conductor of a multilayer electronic component or a multilayer substrate, or a co-firable external conductor and the like is contemplated, a composition, which is not fluidized until the temperature reaches a relatively high temperature, may be selected. For example, use of a material (e.g., lead silicate, zinc borate, alkaline earth metal borate, alkaline earth metal borosilicate, alkaline earth metal silicate, alkali metal borosilicate glasses or the like), which is not fluidized and is present on the surface of the powder to continuously exhibit the antioxidant action until the ceramic layer is densified to some extent, enables co-firing of a base metal conductor and ceramics in an oxidizing atmosphere. In the case of a palladium conductor, oxidation during firing can be retarded, preventing delamination and cracking.

30 [0027] Further, also when there is no problem of oxidation of the metal powder, too early initiation of sintering of the metal powder than the ceramic during the co-firing of the metal powder and the ceramic layer causes uncoincidence of sintering and shrinking behavior between the metal powder and the ceramic, creating structural defects, such as delamination and cracking, and warpage of the multilayer ceramic substrate. In this case, use of a vitreous material, which does not soften until the sintering initiation temperature of the ceramic layer, can inhibit sintering of the metal powder to delay the initiation of sintering, preventing delamination, cracking, etc.

35 [0028] In any of the above cases, after firing, the glass is moved from the surface of the metal powder to the substrate or dielectric layer side and is present in the interface of the substrate or dielectric layer and the conductor film, enhancing the adhesion between the substrate or dielectric layer and the conductor film.

[0029] The presence of glass in a relatively large amount on the surface of the metal powder poses no problem when the metal powder is used for a usual thick film conductor paste. The presence of the glass in an excessively large amount increases the amount of the content of the insulating component in the fired film, often sacrificing the conductivity and solderability of the film and other properties, necessitating proper regulation of the amount of the glass according to applications and necessary properties. In particular, when the metal powder is used for an internal conductor of a multilayer component, the amount of the glass on the surface of the metal powder is preferably as small as possible.

45 [0030] The metal powder having a surface on which a vitreous thin layer is formed is made of noble metal, such as silver, gold, platinum, or palladium, or base metal, such as copper, nickel, cobalt, aluminum, molybdenum, or tungsten and alloy, exception alloys, or mixture thereof. The present invention is particularly useful for an oxidizable metal from the viewpoint of the effect of preventing the oxidation. However, the metal powder is not limited to the oxidizable metal.

50 [0031] The powder of the present invention is prepared by a spray pyrolysis method as claimed. As described in Japanese Patent Publication No. 31522/1988, Japanese Patent Laid-Open Nos. 172802/1994 and 279816/1994 and the like, in the spray pyrolysis method, a solution containing at least one heat-decomposable metal compound is atomized to form fine droplets which are heated at a temperature above the decomposition temperature of the metal compound, preferably a temperature around the melting point of the metal or above to heat-decompose the metal compound, thereby depositing a metal or alloy powder.

55 [0032] This method can provide a metal or alloy powder having good crystallinity, high density, and high dispersibility and can easily control the particle size. In addition, when a precursor of the oxide is previously added to the metal compound solution as a starting solution, the formation of the powder and the coating of the glass can be simultaneously conducted, advantageously eliminating the need to additionally provide the step of coating. That is, the metal powder

prepared by the spray pyrolysis has good crystallinity, has no significant defects in the interior of the metal particle and hardly contains grain boundaries. Therefore, the oxide deposited by the heat decomposition is less likely to deposit in the interior of the metal particle, expelled from the interior of the metal particle, segregated in a high concentration in the vicinity of the surface, and vitrified. The deposited vitreous material relatively evenly covers the surface and, hence, even when it is present in a small amount, can function as a layer for protecting the metal particle against oxidation and sintering. In the spray pyrolysis method, the metal composition of the resultant particles is in agreement with that of the metal composition in the starting solution, making it easy to control the composition, which in turn renders the spray pyrolysis method suitable for the preparation of the powder of the present invention.

[0033] In the process of the present invention, the starting compound of the metal powder may be at least one heat decomposable salt selected from the group consisting of a salt of nitric acid, a salt of sulfuric acid, a chloride, an ammonium complex, a salt of phosphoric acid, a salt of carboxylic acid, a metal alcoholate, and a metal resinate, or a double or complex salt thereof. Use of a mixture of at least two metal salts can offer an alloy or mixed powder.

[0034] The metal compound as the major component is dissolved in water or an organic solvent, an alcohol, acetone or an ether, or a mixed solvent thereof to prepare a solution, and at least one oxide precursor of the vitreous material is added to the solution.

[0035] The oxide precursor used in the present invention produce through heat decomposition an oxide which is hardly dissolved in the metal powder and can be vitrified under metal powder producing conditions according to the present invention. The oxide precursor may be suitably selected from, for example, boric acid, silicic acid, phosphoric acid, various salts of boric acid, silicic acid and phosphoric acid, heat-decomposable salts, such as a nitrate, a sulfate, a chloride, an ammonium complex, a phosphate, a carboxylate, an alcoholate, and a resinate of various metals, and double or complex salts thereof.

[0036] The mixed solution comprised of the metal compound as the major component and the oxide precursor is brought to fine droplets through an atomizer, such as an ultrasonic atomizer or a twinfluid atomizer, followed by heating at a temperature above the decomposition temperatures of the metal compound and the oxide precursor to conduct heat decomposition. Preferably, the heat treatment is conducted at the melting point of the metal as the major component or a higher temperature. However, a temperature about 200°C below the melting point suffices for the expelling effect. In particular, when high density, uniform shape or the like is not required, the heating temperature may be considerably below the melting point. The atmosphere at the time of heating may be suitably selected from oxidizing, reducing and inert atmospheres depending upon the kind of the metal and oxide precursor, heating temperature and the like.

[0037] Regarding the amount of the oxide precursor added, addition of the oxide precursor in an amount of less than 0.01% by weight in terms of oxide based on the metal powder cannot offer any effect. On the other hand, when the amount of the oxide precursor is excessively large, segregation is less likely to occur on the surface. The amount of the oxide precursor added, although it varies depending upon the density of the vitreous material deposited, is preferably up to about 50% by weight from the practical viewpoint. It is particularly preferably in the range of from 0.05 to 20% by weight.

[0038] If necessary, after the formation of the powder, at least a part of the vitreous thin layer deposited on the surface of the powder may be removed by washing, etching or other method to regulate the coverage of the vitreous thin layer.

[0039] Thick film pastes, such as a conductor paste and a resistor paste, comprising the metal powder of the present invention as a conductive component may be prepared by the conventional method. If necessary, other conductive powders and inorganic binders, such as glass powder, and other additives may be incorporated into the metal powder of the present invention.

[0040] The present invention will be described in more detail with reference to the following Examples and Comparative Examples.

Examples 1 to 3

[0041] Nickel nitrate hexahydrate was dissolved in water to a nickel concentration of 50 g/liter, and barium nitrate and boric acid were added to the solution to prepare starting solutions containing barium and boron in terms of BaO and B₂O₃ based on the nickel element specified in Table 1.

[0042] The starting solution thus prepared was brought to fine droplets through an ultrasonic atomizer, and the droplets were fed with the aid of a gas, regulated to have a weakly reducing property, as a carrier into a ceramic tube heated to 1,400°C in an electric furnace. The droplets were heat decomposed in the course of passing through a heating zone to prepare a nickel powder containing barium oxide and boron oxide.

[0043] The resultant powders were collected and analyzed by X-ray diffractometry. As a result, for all the powders, any diffraction line other than diffraction lines derived from nickel and a very small amount of nickel oxide was not detected. When the powder was washed with a 5% dilute hydrochloric acid, dissolution of nickel hardly occurred, whereas the amount of the additives in the powder after the washing was reduced by at least 80%. This indicates that

the added barium and boron are segregated in a high concentration on the surface of the nickel particles and, as analyzed by X-ray diffractometry, are found to be present in the state of amorphous $\text{BaO-B}_2\text{O}_3$ glass.

[0044] The oxidation initiating temperature and the sintering initiating temperature of the powder were evaluated by thermogravimetry (TG) in the air and by thermomechanical analysis (TMA) in a reducing atmosphere, and the results are given in Table 1. The oxidation initiation temperature is the temperature necessary for providing a 1% weight increase in the TG measurement. The sintering initiation temperature is the shrinking initiation temperature in the TMA measurement.

Comparative Example 1

[0045] A pure nickel powder was prepared in the same manner as in Example 1, except that neither barium nitrate nor boric acid was added. The properties of the resultant powder are given in Table 1.

[0046] Comparison of the results of Examples 1 to 3 with the results of Comparative Example 1 shows that the presence of $\text{BaO-B}_2\text{O}_3$ glass increases the oxidation initiation temperature by 50 to 240°C, confirming the effect of improving the oxidation resistance. Further, the sintering initiation temperature also is increased by 220 to 250°C to 590 to 620°C, indicating that since the softening point of the $\text{BaO-B}_2\text{O}_3$ glass having this composition is 600 to 610°C, the sinterability of the powder can be regulated by varying the softening point of the vitreous material.

Example 4

[0047] A nickel powder having a $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass on the surface thereof was prepared in the same manner as in Example 1, except that calcium nitrate tetrahydrate, aluminum nitrate nonahydrate, and boric acid in respective amount in terms of CaO , Al_2O_3 , and B_2O_3 based on the nickel element as specified in Table 1 were added.

[0048] The oxidation initiation temperature and the sintering initiation temperature were measured in the same manner as in Example 1, and the results are also given in Table 1. As a result, the sintering initiation temperature as measured by TMA was 770°C, while the softening point of $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass having this composition was 735 to 800°C, here again indicating that the sinterability of the powder can be regulated by varying the softening point of the vitreous material.

Example 5

[0049] A nickel powder having a BaO-SiO_2 glass on the surface thereof was prepared in the same manner as in Example 1, except that barium nitrate, tetraalkoxysilane, and an alcohol, for dissolving the tetraalkoxysilane, in respective amounts specified in Table 1 were added.

[0050] The oxidation initiation temperature and the sintering initiation temperature are also given in Table 1.

Example 6

[0051] Copper nitrate trihydrate was dissolved in water to a copper concentration of 50 g/liter, and barium nitrate and boric acid in respective amounts in terms of $\text{BaO-B}_2\text{O}_3$ based on the copper element as specified in Table 1 were added to prepare starting solutions. The procedure of Example 1 was repeated to bring the solution to fine droplets, followed by heat decomposition at 1,100°C to prepare a copper powder with $\text{BaO-B}_2\text{O}_3$ glass present on the surface thereof.

[0052] The oxidation initiation temperature and the sintering initiation temperature of the resultant powder are given in Table 1.

Comparative Example 2

[0053] A pure copper powder was prepared in the same manner as in Example 6, except that neither barium nitrate nor boric acid was added.

[0054] The oxidation initiation temperature and the sintering initiation temperature are given in Table 1.

Table 1

	Metal powder	Additive element and amount of additive element added based on metal powder (in terms of oxide, wt%)		Oxidation initiation temperature (°C)	Sintering initiation temperature (°C)
Ex. 1	Ni	Ba 0.05	B 0.02	440	590
Ex. 2	Ni	Ba 0.40	B 0.70	530	620
Ex. 3	Ni	Ba 3.90	B 7.10	630	590
Ex. 4	Ni	Ca 6.00	Al 3.00 B 1.00	550	770
Ex. 5	Ni	Ba 0.50	Si 0.50	450	750
Comparative Ex. 1	Ni	-	-	390	370
Ex. 6	Cu	Ba 4.00	B 6.00	510	600
Comparative Ex. 2	Cu	-	-	300	310

[0055] In the metal powder having a vitreous thin layer on the surface thereof according to the present invention, even in the case of an easily oxidizable metal, such as a base metal, oxidation during storage and firing of the paste can be effectively prevented.

[0056] In particular, selection of glass, which is not fluidized until the temperature becomes high, enables even a base metal paste to be fired in an oxidizing atmosphere throughout the whole step, realizing a low cost and eliminating the need to carefully control the atmosphere and the temperature. This enables the preparation of a product which, even when used in a multilayer component, causes no deteriorated dielectric properties and has high reliability.

[0057] Further, selection of the composition of the vitreous material enables functions, such as retardation or acceleration of the sintering of the paste and improvement in adhesion, to be properly regulated, realizing the preparation

of a conductor film having excellent adhesion without sacrificing the conductivity, solderability and other properties. Since the vitreous material is fluidized and removed from the surface of the powder after the sintering, the influence on the properties is lower than that in the conventional coating or addition of an oxide.

[0058] Further, when the paste and the ceramic are co-fired, the glass can serve to prevent the oxidation and, in addition, serve as a layer for protecting the metal powder against sintering. Bringing the shrinking behavior in sintering of the metal powder to that of the ceramic layer enables the preparation of a multilayer component and a multilayer substrate free from a structural defect.

[0059] Further, according to the spray pyrolysis method used in the present invention, when a glass forming component is previously added to a starting solution, metal powders having vitreous thin layers of various compositions can be simply prepared in one-stage spray pyrolysis.

Claims

1. A process for preparing a metal powder having a vitreous thin layer on at least part of the surface thereof, said process comprising the steps of: bringing a solution comprising at least one heat-decomposable metal compound to fine droplets; and heating the droplets to a temperature above the decomposition temperature of the metal compound, wherein at least one precursor of an oxide, heat-decomposable to produce a vitreous material which, together with the metal, does not form a solid solution, is added to the solution and the vitreous material is deposited, upon the heating, in the vicinity of the surface of the metal powder.
2. A metal powder prepared according to the process of claim 1 and having a vitreous thin layer on at least part of the surface thereof, wherein the metal powder is selected from the group consisting of a noble metal, copper, nickel, cobalt, aluminum, molybdenum, or tungsten and alloys, except iron alloys, or mixtures thereof.
3. A metal powder according to claim 2, wherein the compound forming the vitreous thin layer is at least one member selected from oxides of silicon, boron, phosphorus, germanium, tin, lead, bismuth, alkali metals, alkaline earth metals, copper, zinc, cadmium, aluminum, indium, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rare earth elements, iron, and cobalt.
4. The metal powder according to claim 2 or 3, wherein the amount of the vitreous thin layer is 0.01 to 50 % by weight based on the metal powder, excluding the vitreous thin layer.
5. A conductor paste comprising the metal powder according to claims 2 to 4.
6. A multilayer ceramic electronic component comprising a conductor layer formed using the conductor paste according to claim 5.
7. A multilayer ceramic substrate comprising a conductor layer formed using the conductor paste according to claim 5.

Patentansprüche

1. Verfahren zur Herstellung eines Metallpulvers mit einer glasartigen dünnen Schicht auf zumindest einem Teil seiner Oberfläche, wobei dieses Verfahren folgende Schritte umfasst:
 Überführung einer Lösung, die mindestens eine durch Wärme zersetzbare Metallverbindung umfasst, in feine Tröpfchen
 und Erhitzen der Tröpfchen auf eine Temperatur über der Zersetzungstemperatur der Metallverbindung,
 wobei der Lösung mindestens ein Vorläufer eines Oxids, der durch Wärme zersetzbar ist, um ein glasartiges Material zu erzeugen, das zusammen mit dem Metall keine feste Lösung bildet, zugesetzt wird und das glasartige Material beim Erhitzen in der Nähe der Oberfläche des Metallpulvers abgeschieden wird.
2. Metallpulver, das nach dem Verfahren von Anspruch 1 hergestellt wird und eine glasartige dünne Schicht auf mindestens einem Teil seiner Oberfläche aufweist, wobei das Metallpulver aus der aus einem Edelmetall, Kupfer, Nickel, Cobalt, Aluminium, Molybdän oder Wolfram und Legierungen mit Ausnahme von Eisenlegierungen oder

EP 0 834 370 B1

deren Mischungen bestehenden Gruppe ausgewählt wird.

3. Metallpulver nach Anspruch 2, worin die die glasartige dünne Schicht bildende Verbindung mindestens eine aus den Oxiden von Silicium, Bor, Phosphor, Germanium, Zinn, Blei, Wismut, Alkalimetallen, Erdalkalimetallen, Kupfer, Zink, Cadmium, Aluminium, Indium, Titan, Zirkonium, Vanadium, Niob, Tantal, Chrom, Molybdän, Wolfram, Mangan, Seltenerdelementen, Eisen und Cobalt ausgewählte Verbindung ist.
4. Metallpulver nach Anspruch 2 oder 3, worin die Menge der glasartigen dünnen Schicht bezogen auf das Metallpulver ohne die glasartige dünne Schicht 0,01 bis 50 Gew.-% ausmacht.
5. Leiterpaste, die das Metallpulver nach Anspruch 2 bis 4 umfasst.
6. Mehrschichtige keramische Elektronikkomponente, die eine unter Verwendung der Leiterpaste von Anspruch 5 hergestellte Leiterschicht umfasst.
7. Mehrschichtiges Keramiksubstrat, das eine unter Verwendung der Leiterpaste von Anspruch 5 hergestellte Leiterschicht umfasst.

Revendications

1. Procédé pour la préparation d'une poudre métallique ayant une couche mince vitreuse sur au moins une partie de sa surface, ledit procédé comprenant les étapes consistant : à transformer en fines gouttelettes une solution comprenant au moins un composé métallique décomposable à la chaleur ; et à chauffer les gouttelettes à une température supérieure à la température de décomposition du composé métallique, procédé dans lequel on ajoute à la solution au moins un précurseur d'un oxyde, décomposable à la chaleur pour produire une substance vitreuse qui, conjointement avec le métal, ne forme pas une solution solide, et sous l'effet de la chaleur, la substance vitreuse se dépose de façon adjacente à la surface de la poudre métallique.
2. Poudre métallique préparée selon le procédé de la revendication 1 et ayant une couche mince vitreuse sur au moins une partie de sa surface, dans laquelle la poudre métallique est choisie dans le groupe constitué par un métal précieux, le cuivre, le nickel, le cobalt, l'aluminium, le molybdène ou le tungstène et leurs alliages, sauf les alliages du fer, ou des mélanges de ceux-ci.
3. Poudre métallique selon la revendication 2, dans laquelle le composé formant la couche mince vitreuse est au moins une substance choisie parmi les oxydes de silicium, de bore, de phosphore, de germanium, d'étain, de plomb, de bismuth, de métaux alcalins, de métaux alcalino-terreux, de cuivre, de zinc, de cadmium, d'aluminium, d'indium, de titane, de zirkonium, de vanadium, de niobium, de tantale, de chrome, de molybdène, de tungstène, de manganèse, d'éléments des terres rares, de fer et de cobalt.
4. Poudre métallique selon la revendication 2 ou 3, dans laquelle la proportion de la couche mince vitreuse est de 0,01 à 50 % en poids par rapport à la poudre métallique, à l'exclusion de la couche mince vitreuse.
5. Pâte conductrice comprenant la poudre métallique selon les revendications 2 à 4.
6. Composant électronique céramique multicouches, comprenant une couche conductrice formée avec la pâte conductrice selon la revendication 5.
7. Substrat céramique multicouches, comprenant une couche conductrice formée avec la pâte conductrice selon la revendication 5.